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**LIQUID RAW INGREDIENT FEEDING DEVICE FOR THE CVD**

[CVD Yo Ekitai Genryo Kyokyu Sochi]

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(54) Title of the invention

Liquid raw ingredient feeding device for the CVD

(57) Summary

Objective: To provide a liquid raw ingredient feeding device for the CVD which is capable of continuously feeding a liquid raw ingredient at a constant quantitative ratio, of improving the film formation efficiency, and of forming a thin film (e.g., oxide superconductor thin film, etc.) with stable attributes (e.g., film quality, etc.).

Solution mechanism: The liquid raw ingredient feeding device (30) for the CVD constituted to possess the cylindrical raw ingredient solution feeding unit (31), wherein a liquid raw ingredient is scheduled to be fed into the interior thereof, the cylindrical and distally tapered atomizing gas feeding unit (32), which is configured to surround the outer circumference of said feeding unit (31) and which feeds an atomizing gas for atomizing the aforementioned liquid raw ingredient into a gap between itself and the aforementioned raw ingredient solution feeding unit (31), and the cylindrical shield gas feeding unit (33), which is configured to surround the outer circumference of said atomizing gas feeding unit (32) and which feeds a shield gas for cooling and shielding both the raw ingredient solution feeding unit (31) and

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<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

the atomizing gas feeding unit (32) into a gap between itself and the atomizing gas feeding unit (32).

#### Patent Claims

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##### Claim 1

A liquid raw ingredient feeding device for the CVD characterized by the possession of a cylindrical raw ingredient solution feeding unit wherein a liquid raw ingredient is scheduled to be fed into the interior thereof and a cylindrical and distally tapered atomizing gas feeding unit which is configured to surround the outer circumference of said feeding unit and which feeds an atomizing gas for atomizing the aforementioned liquid raw ingredient into a gap between itself and the aforementioned raw ingredient solution feeding unit.

##### Claim 2

A liquid raw ingredient feeding device for the CVD specified in Claim 1 characterized by a constitution wherein a cylindrical shield gas feeding unit is configured to surround the outer circumference of the aforementioned atomizing gas feeding unit for the purpose of feeding a shield gas which cools and shields the aforementioned raw ingredient solution feeding unit and the aforementioned atomizing gas feeding unit into a gap between itself and the aforementioned atomizing gas feeding unit.

##### Claim 3

A liquid raw ingredient feeding device for the CVD specified in Claim 1 or 2 characterized by the fact that a liquid reservoir for temporarily stocking the liquid raw ingredient is configured within the aforementioned raw ingredient solution feeding unit.

Detailed explanation of the invention

[0001]

(Technical fields to which the invention belongs)

The present invention concerns a liquid raw ingredient feeding device for the CVD which is orchestrated on a thin film formation device for forming above a substrate an oxide material (e.g., oxide superconductor, etc.) based on the chemical vapor phase deposition method (hereafter referred to as the "CVD method").

[0002]

(Prior art)

In recent years, oxide superconductors such as the Y-Ba-Cu-O type, Bi-Sr-Ca-Cu-O type, Tl-Ba-Ca-Cu-O type, etc. have been discovered as oxide superconductors the critical temperatures ( $T_c$ ) of which are higher than the liquid nitrogen temperature (approximately 77 K). Various studies, furthermore, are being conducted on thin films of these oxide superconductors in anticipation of their applications to such fields as electric power cables, magnets, energy storage materials, electric power

generators, medical and therapeutic machines, electric current leads, etc. One known method for manufacturing such oxide superconductors is a method wherein an oxide superconductor thin film is formed on the surface of a substrate based on a thin film formation mechanism such as the chemical vapor phase deposition method (CVD method), etc. It is known that oxide superconductor thin films formed by this type of thin film formation mechanism are endowed with high critical current densities ( $J_c$ ) and exhibit excellent superconductive performances. Of all CVD methods, furthermore, a CVD method which uses an organic metal compound (e.g., metal complex, metal alkoxide, etc.) as a raw ingredient has captured attention as a mechanism which is capable, based on a high film formation rate, of forming a thicker film within a brief period.

[0003]

As far as such methods for manufacturing oxide superconductors based on the CVD method are concerned,  $\beta$ -diketone compounds or cyclopentadienyl compounds of the respective elements that constitute the oxide superconductors are normally used as raw ingredient compounds, and in a case where an oxide superconductor of the Y-Ba-Cu-O type is manufactured, for example, organic metal complex raw ingredients (MO raw ingredients) such as  $Y(thd)_3$ ,  $Ba(thd)_2$  and/or  $Ba(thd)_2 \cdot phen_2$ ,  $Cu(thd)_2$ , etc. ( $thd = 2,2,6,6$ -tetramethyl-3,5-heptanedione) are being used. These organic metal complex raw ingredients are materials which are solid at room temperature, and they exhibit conspicuous sublimating properties

in cases where they are heated at 200 ~ 300°C, but it is difficult to control the compositions of these raw ingredients in that the sublimating efficiencies radically differ depending on their purities or on the surface area variations of the fed raw ingredients during the heating period, due to which these solid complex raw ingredients have been used as liquid raw ingredients after having been solubilized into organic solvents such as tetrahydrofuran (THF), isopropanol, toluene, diglyme (2,5,8-trioxononane), etc.

[0004]

As will be discussed on a later occasion, these liquid raw ingredients are fed, after having been heated and vaporized within a vaporizer, into a reaction chamber together with a carrier gas, and after a chemical reaction has been induced within said reaction chamber, the resulting reaction product is deposited on the surface of a substrate installed within said reaction chamber, as a result of which the objective Y-Ba-Cu-O-type oxide superconductor becomes obtained. Incidentally, in a case where a solution obtained by solubilizing an organic metal complex raw ingredient into an organic solvent is used as a liquid raw ingredient for the CVD, devices for feeding such liquid raw ingredients for the CVD have been problematic.

[0005]

Figure 7 shows an apparatus for manufacturing an oxide superconductor equipped with a liquid raw ingredient-feeding device of the prior art for the CVD as it is used for

manufacturing the oxide superconductor. This apparatus for manufacturing an oxide superconductor is constituted approximately by the CVD reaction device (1), the liquid raw ingredient feeding device (3) for the CVD, the vaporizer (4), and the raw liquid feeding device (5). The aforementioned CVD reaction device (1) possesses the reaction chamber (2), which constitutes a CVD reaction & generation chamber, the substrate transportation device (7), which transports the long substrate (6) on which an oxide superconductor layer is scheduled to be formed, and the nozzle (8), whereas the vacuum pump (9) is also connected to the same, whereas the heater (10), which heats the substrate (6) by heating the entire reaction chamber (1) [sic: Presumably "(2)"] is configured on the exterior of the same. The liquid raw ingredient-feeding device (3) is connected, via the connection tube (11), to the aforementioned nozzle (8), whereas the oxygen gas-feeding source (13) is connected, via the connection tube (12), to the same.

[0006]

The liquid raw ingredient feeding device (3) is constituted, as Figure 8 shows, mainly by the cylindrical feeding unit (14), the needle (16), which is characterized by an injection needle shape and which has been inserted into the feeding unit (14) up to nearly the bottom (15) thereof, the capillary tube (17), which is configured to punch through the aforementioned bottom (15) and which links the feeding unit (14) and the vaporizer (5) [sic: Presumably "vaporizer (4)" or "raw liquid feeding device (5)"],



the cylindrical suction unit (18), which blankets the bottom side of the aforementioned feeding unit (14), and the suction tube (19), which is connected to the profile portion of said suction unit (18). The carrier gas (e.g., gaseous argon, etc.) feeding source (21) is connected, via the connection tube (20), to the aforementioned feeding unit (14). The vaporizer (5) [sic] is connected to the lower end of the suction unit (18) of this liquid raw ingredient feeding device (3). The raw liquid feeding device (5) is connected, via the needle (16) and the tube (23), to the liquid raw ingredient feeding device (3) as well.

[0007]

The vaporizer (5) [sic] is characterized by the shape of a container, whereas the heater (22), which heats and vaporizes the liquid raw ingredient at a desired temperature by heating the interior of the vaporizer (5) [sic] is auxiliary configured on the outer circumference of the same. The raw liquid feeding device (5) possesses the tubular pump (24) and the storage container (25), whereas the liquid raw ingredient (26), which has been obtained by solubilizing the aforementioned organic metal complex into an organic solvent, is stored within the storage container (25). The aforementioned tubular pump (24) is constituted by configuring the tube (23) along the outer circumference of the major roller (27) and by configuring, in freely rotatable fashions, multiple minor rollers on the exterior of said tube (23), whereas the flexible tube (23) is progressively

pressurized by the respective minor rollers (28), ... by rotating said minor rollers (28), etc. based on a power transmitted from a drive source (not shown in the figure), based on which the liquid raw ingredient (26) within the tube (23) can be discharged into the feeding unit (14) via the needle (16).

[0008]

In a case where a long oxide superconductor is manufactured by using the apparatus for manufacturing an oxide superconductor equipped with such a liquid raw ingredient feeding device of the prior art, the long substrate (6) is transported into the reaction chamber (2) by the substrate transportation device (7), and furthermore, the liquid raw ingredient (26) is continuously fed, via the needle (16), into the feeding unit (14) of the liquid raw ingredient feeding device (3) at a certain flow rate by the tubular pump (24). In such a case, the liquid raw ingredient (26) is stocked within the feeding unit (14) at a certain depth, whereas the interior of the reaction chamber (2) is depressed at several Torr by heating the vaporizer (4), whereas the carrier gas is fed into the feeding unit (14) from the carrier gas feeding source (21).

[0009]

As a result, a depressed state of several Torr also becomes achieved within the vaporizer (4), and the liquid raw ingredient (26) within the feeding unit (14) becomes fed into the vaporizer (4) along the flow of the carrier gas. In such a case, the liquid

raw ingredient (26) within the feeding unit (14) flows, as Figure 9 shows, downward to the lower end of the capillary tube (17) from a diagonally cut open plane at the distal end of the capillary tube (17) along the inner wall of the same, as a result of which a liquid droplet becomes formed on said lower end under the pervasion of surface tension, and as said liquid droplet has become enlarged to a certain size, it drops into the vaporizer (4). The thus dropping liquid raw ingredient (26) of the liquid droplet shape reaches the bottom of the vaporizer (4), and after it has subsequently become vaporized and then fed, via the connection tube (11), into the reaction chamber (2), it forms a raw ingredient gas atmosphere. Immediately thereafter, the long substrate (6) within the reaction chamber (2) is heated by the heater (10) for inducing the reaction of the surrounding raw ingredient, and after an oxide superconductor thin film has been deposited on the surface of said substrate (6), the objective oxide superconductor becomes manufactured.

[0010]

(Problems to be solved by the invention)

In a case where the liquid raw ingredient (26) is fed by using the liquid raw ingredient feeding device (3) of the prior art, however, the liquid raw ingredient (26) drops only after it has formed a liquid droplet of a certain size at the lower end of the capillary tube (17), due to which it is impossible to feed the liquid raw ingredient (26) into the vaporizer (4) at a constant

quantitative ratio, which is problematic in that the raw ingredient gas also becomes fed into the reaction chamber (2) in a periodically pulsated fashion. Incidentally, it is necessary to manage the pressure and temperature within the reaction chamber (2) at constant levels from the standpoint of forming an oxide superconductor film of a favorable quality, but in a case where the raw ingredient gas becomes fed into the reaction chamber (2) in a periodically pulsated fashion, the pressure and temperature within the reaction chamber (2) inevitably fluctuate, which is problematic in that it becomes impossible to obtain a favorable oxide superconductor thin film with stable quality and superconductive performances along the lengthwise direction of the substrate (6). Even in a case where the rate for feeding the liquid raw ingredient (26) into the vaporizer (4) is elevated for the purpose of upgrading the film formation efficiency of the liquid raw ingredient feeding device (3) of the prior art, furthermore, the film formation efficiency becomes saturated at a certain critical rate, due to which the film formation efficiency is unsatisfactory.

[0011]

The objective of the present invention, which has been conceived in acknowledgment of the aforementioned backdrop, is to provide a liquid raw ingredient feeding device for the CVD which is capable of continuously feeding a liquid raw ingredient at a constant quantitative ratio, of improving the film formation efficiency, and of forming a thin film (e.g., oxide superconductor

thin film, etc.) with stable attributes (e.g., film quality, etc.).

[0012]

(Mechanism for solving the problems)

The invention specified in Claim 1 provides, as a mechanism for solving the aforementioned problems, a liquid raw ingredient feeding device for the CVD characterized by the possession of a cylindrical raw ingredient solution feeding unit wherein a liquid raw ingredient is scheduled to be fed into the interior thereof and a cylindrical and distally tapered atomizing gas feeding unit which is configured to surround the outer circumference of said feeding unit and which feeds an atomizing gas for atomizing the aforementioned liquid raw ingredient into a gap between itself and the aforementioned raw ingredient solution feeding unit.

[0013]

The invention specified in Claim 2, furthermore, provides, as a mechanism for solving the aforementioned problems, a liquid raw ingredient feeding device for the CVD specified in Claim 1 characterized by a constitution wherein a cylindrical shield gas feeding unit is configured to surround the outer circumference of the aforementioned atomizing gas feeding unit for the purpose of feeding a shield gas which cools and shields the distal end of the aforementioned raw ingredient solution feeding unit and the distal end of the aforementioned atomizing gas feeding unit into a gap between itself and the aforementioned atomizing gas feeding unit.

The invention specified in Claim 3, furthermore, provides, as a mechanism for solving the aforementioned problems, a liquid raw ingredient feeding device for the CVD specified in Claim 1 or 2 characterized by the fact that a liquid reservoir for temporarily stocking the liquid raw ingredient is configured within the aforementioned raw ingredient solution feeding unit.

[0014]

(Application embodiments of the invention)

In the following, an example of the liquid raw ingredient feeding device of the present invention for the CVD will be explained with reference to figures. Figure 1 shows an example of apparatus for manufacturing an oxide superconductor equipped with the liquid raw ingredient feeding device of the present invention for the CVD. This apparatus for manufacturing an oxide superconductor is constituted approximately by the liquid raw ingredient feeding device (30) for the CVD, the raw liquid feeding device (40), the vaporizer (50), and the CVD reaction device (60).

[0015]

The liquid raw ingredient feeding device (30) is characterized, as Figure 2 shows, by a threefold structure constituted approximately by the cylindrical raw ingredient solution feeding unit (31), the cylindrical and distally tapered atomizing gas feeding unit (32), which is configured to surround the outer circumference of said feeding unit (31), and the cylindrical shield gas feeding unit (33), which is configured to

surround the outer circumference of said atomizing gas feeding unit (32) with the exception of the distal end thereof.

[0016]

The liquid raw ingredient (34), which has been pumped from the raw liquid feeding device (40), which will be discussed on a later occasion, is scheduled to become fed into the interior of the raw ingredient solution feeding unit (31), whereas the liquid reservoir (35) for temporarily stocking the fed liquid raw ingredient (34) is configured at the center of the former. The inner diameter of this liquid reservoir (35) is designed to be larger than the respective inner diameters of the distal ends of the upper and lower portions of the raw ingredient solution feeding unit (31) in such a way that the liquid raw ingredient (34) pumped from the raw liquid feeding device (40) will become continuously fed into the distal end of the same while being concomitantly stocked. By virtue of the configuration of said liquid reservoir (35), even if bubbles, etc. migrate into the liquid raw ingredient (34), said bubbles, etc. become afloat on the surface of the liquid raw ingredient (34) being stocked in the liquid reservoir (35), and their arrival at the distal end can accordingly be prevented.

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[0017]

The atomizing gas feeding unit (32) is scheduled to feed an atomizing gas for atomizing the aforementioned liquid raw ingredient (34) into the gap vis-à-vis the raw ingredient solution

feeding unit (31). The atomizing gas feeding source (36) is connected, via the atomizing gas MFC (36a), to the upper portion of the atomizing gas feeding unit (32) for enabling the feeding of the atomizing gas into the atomizing gas feeding unit (32). Atomizing gases usable in this context are concretely instantiated by gaseous argon, gaseous helium, gaseous nitrogen, etc. As far as the liquid raw ingredient feeding device (30) of this example is concerned, the nozzle (37) is constituted by the distal end of the atomizing gas feeding unit (32) and the distal end of the raw ingredient solution feeding unit (31).

[0018]

The shield gas feeding unit (33) is designed to feed a shield gas into the gap vis-à-vis the atomizing gas feeding unit (32) for purposes of cooling the aforementioned atomizing gas feeding unit (32) and of shielding the nozzle (37). The tapered unit (38), which protrudes outward, is configured on a site underneath the center of the shield gas feeding unit (33). The shield gas feeding source (39), furthermore, is connected, via the shield gas MFC (39a), to the upper portion of the shield gas feeding unit (33) and is thus constituted to feed the shield gas into the shield gas feeding unit (33). Shield gases usable in this context are concretely instantiated by gaseous argon, gaseous helium, gaseous nitrogen, etc.

[0019]

As far as the liquid raw ingredient feeding device (30) of the aforementioned constitution is concerned, in a case where the



liquid raw ingredient (34) is pumped into the raw ingredient solution feeding unit (31) at a constant flow rate and where the atomizing gas is pumped into the atomizing gas feeding unit (32) at a constant flow rate, the liquid raw ingredient (34) becomes stocked within the liquid reservoir (35) and concomitantly reaches the distal end of the raw ingredient solution feeding unit (31), whereas since the atomizing gas is orchestrated to flow from the distal end of the atomizing gas feeding unit (32) outside said distal end, the liquid raw ingredient (34) becomes instantly atomized by the aforementioned atomizing gas in a case where it becomes blown out of the nozzle (37), based on which a constant quantitative ratio of the misty liquid raw ingredient (34) can be continuously fed into the vaporizer (50). In a case where the shield gas is concomitantly pumped into the shield gas feeding unit (33) at a constant flow rate, furthermore, both the atomizing gas feeding unit (32) and the raw ingredient solution feeding unit (31) become cooled, due to which the liquid raw ingredient (34) flowing within said raw ingredient solution feeding unit (31) becomes concomitantly cooled, based on which the vaporization of the liquid raw ingredient (34) midway can be prevented. Since the shield gas flows outside the nozzle (37) from the distal end of the shield gas feeding unit (33) above the same, furthermore, the surroundings of the nozzle (37) become shielded by the shield gas, based on which the adhesion, to the nozzle (37), of the raw ingredient gas generated as a result of the vaporization, within

the vaporizer (50), of the liquid raw ingredient (34) and its secondary deposition as a solid raw ingredient can be prevented.

[0020]

The raw liquid feeding device (40) is connected, via the connection tube (41) equipped with the liquid raw ingredient MFC (41a), to the raw ingredient solution feeding unit (31) of said liquid raw ingredient feeding device (30). One the chemical resistance of which is excellent (e.g., a pipe the inner plane of which is coated with a fluorinated resin, etc.) is used as said connection tube (41). The raw liquid feeding device (40) possesses the storage container (42) and the compression source (43), whereas the liquid raw ingredient (34) is stored within the interior of the storage container (42). One the chemical resistance of which is excellent (e.g., glass bottle, etc.) is used as the storage container (42). The aforementioned compression source (43) is designed to compress the interior of the storage container (42) by feeding gaseous He, etc. into the storage container (42) and to induce the discharge of the liquid raw ingredient (34) that has filled the storage container (42) into the connection tube (41) at a constant flow rate.

[0021]

The liquid raw ingredient (34) stored within the storage container (42) is obtained by solubilizing into an organic solvent a mixture of multiple types of organic metal compounds (e.g., organic metal complexes and/or metal alkoxides of the constituent metal elements of the objective compound targeted for film

formation) the compositional ratio of which coincides with that of the objective compound. These organic metal compounds and organic solvents are concretely instantiated by organic metal complexes used in a case where a film of a Y-Ba-Cu-O-type oxide superconductor is formed such as  $\text{Y(thd)}_3$ ,  $\text{Ba(thd)}_2$  and/or  $\text{Ba(thd)}_2\text{phen}_2$ ,  $\text{Cu(thd)}_2$ , etc. (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) and organic solvents such as tetrahydrofuran (THF), isopropanol, toluene, diglyme (2,5,8-trioxononane), etc.

[0022]

A vaporizer (50) characterized by the shape of a container, on the other hand, is configured underneath the liquid raw ingredient feeding device (30), whereas the distal end of the central portion of the liquid raw ingredient feeding device (30) is stored within said vaporizer (50), based on which the liquid raw ingredient feeding device (30) and the vaporizer (50) become mutually connected. The heater (51), which serves a function of heating the interior of the vaporizer (50), is auxiliary configured on the outer circumference of said vaporizer (50), whereas the misty liquid raw ingredient (34) sprayed from the aforementioned nozzle (37) is heated at a certain temperature and vaporized by said heater (51), as a result of which a raw ingredient gas becomes obtained. This vaporizer (50) is connected, via the transportation tube (53), to the CVD reaction device (60).

[0023]

This CVD reaction device (60) possesses the reaction chamber (61) made of quartz, whereas this reaction chamber (61), which is characterized by a horizontally elongated cylindrical shape wherein both ends thereof are closed, is compartmentalized, by partition walls (not shown in the figure), into the substrate introduction unit (62), the reaction & generation chamber (63), and the substrate exit unit (64) in proper order from the left in Figure 1. An introduction hole for introducing the tape-shaped substrate (65), furthermore, is formed on the substrate introduction unit (62), whereas an exit hole for exporting the substrate (65) is formed on the substrate exit unit (64), whereas, though omitted from the figure, sealing components which seal the respective gaps of the introduction hole and exit hole in a state where the substrate (65) is being transmitted for the purpose of maintaining the substrate introduction unit (62) and substrate exit unit (64) in hermetic states are configured on the circumferential fringes of said holes. The triangular gas diffusion unit (66), which is linked to the reaction & generation chamber (63), furthermore, is attached to the ceiling portion of the reaction & generation chamber (63).

[0024]

The heater (47), which covers a region ranging from the portion of the substrate introduction unit (62) toward the reaction & generation chamber (63) side to the portion of the substrate exit unit (64) toward the reaction & generation chamber (63) side, on the other hand, is configured on the exterior of the

CVD reaction device (60), whereas the substrate introduction unit (62) and the substrate exit unit (64) are connected respectively to the inert gas feeding source (68) and the oxygen gas feeding source (69). The transportation tube (53), which is connected to the raw ingredient gas vaporizer (50), furthermore, is connected to the gas diffusion unit (66). A heating mechanism (omitted from the figure) which serves a function of preventing the deposition of the raw ingredient gas in the form of the liquid raw ingredient (34) is configured around said transportation tube (53). Incidentally, the oxygen gas feeding source (54) is constituted to become branched and connected to an intermediate portion of the transportation tube (53) and to feed gaseous oxygen into the transportation tube (53).

[0025]

The gas exhaustion tube (70), furthermore, is configured on the bottom of the aforementioned CVD reaction device (60) and is connected to the pressure adjustment device (72) equipped with the vacuum pump (71) for exhausting the gas within the CVD reaction device (60). The substrate transportation mechanism (75), which consists of the tension drum (73) and the winding drum (74) for collecting the substrate (65) being transmitted through the CVD reaction device (60), are additionally configured on the profile side of the CVD reaction device (60) toward the substrate exit unit (64). The substrate transportation mechanism (78), which consists of the tension drum (76) and the exporting drum (77) for

feeding the substrate (65) into the CVD reaction device (60), furthermore, is configured on the profile side of the same toward the substrate introduction unit (62).

[0026]

Next, a case where an oxide superconductor is manufactured by feeding, into the reaction chamber (61), a raw ingredient gas obtained as a result of the vaporization of the liquid raw ingredient (34) under the pervasion of the apparatus for manufacturing an oxide superconductor equipped with the liquid raw ingredient feeding device of the aforementioned constitution and by then forming an oxide superconductor thin film on the tape-shaped substrate (65) within the reaction chamber (61) will be explained.

[0027]

In the context of manufacturing an oxide superconductor by using the manufacturing apparatus shown in Figure 1, the tape-shaped substrate (65) and the liquid raw ingredient (34) are prepared first. A dimensionally elongated one is used as said substrate (65), and one obtained by coating an intermediate layer made of a ceramic on the upper plane of a heat-resistant metallic tape with a low thermal expansion coefficient is especially desirable as said substrate (65). Metallic materials or alloys such as silver, platinum, stainless steel, copper, Hastelloy (C276, etc.), etc. are desirable as the constituent materials of the aforementioned heat-resistant metallic tape. Apart from the aforementioned metallic tapes, furthermore, various glass tapes or

tapes constituted by various ceramics (e.g., mica tape, etc.) may also be used. Next, ceramics the thermal expansion coefficients of which are closer to those of oxide superconductors than to those of metals such as YSZ (yttrium-stabilized zirconia),  $\text{SrTiO}_3$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{LaAlO}_3$ ,  $\text{LaGaO}_3$ ,  $\text{YAlO}_3$ ,  $\text{ZrO}_2$ , etc. are desirable as the constituent materials of the aforementioned intermediate layer, and of these, it is especially desirable to use ones the crystal orientations of which are as uniform as possible.

[0028]

Next, one obtained by solubilizing into an organic solvent (e.g., THF, etc.) a mixture of multiple types of organic metal compounds (e.g., organic metal complexes and/or metal alkoxides of the constituent metal elements of the objective compound targeted for film formation) the compositional ratio of which coincides with that of the objective compound can be used as the liquid raw ingredient (34), from which the oxide superconductor is scheduled to be generated by means of a CVD reaction. After said liquid raw ingredient (34) has been prepared, it is filled into the raw liquid feeding device (40).

[0029]

Once the aforementioned substrate (65) has become prepared, it is not only fed into the reaction chamber (61) from the substrate introduction unit (62) at a certain transportation rate by the substrate transportation mechanism (78) but also wound by the winding drum (74) of the substrate transportation mechanism (75), and furthermore, the substrate (65) within the reaction &

generation chamber (63) is heated at a certain temperature by the heater (47). Incidentally, it is desirable to clean, prior to the importation of the substrate (65), the interior of the reaction chamber (61) by expelling unnecessary gases (e.g., air, etc.) there from by feeding an inert gas, as a purge gas, into the reaction chamber (61) from the inert gas feeding source (68) and by concomitantly activating the pressure adjustment device (72) for suctioning the gases within the reaction chamber (61).

[0030]

Once the substrate (65) has become imported into the reaction chamber (61), gaseous oxygen is pumped into the reaction chamber (61) from the oxygen gas feeding source (69), and furthermore, the liquid raw ingredient (34) is pumped, at a flow rate of approximately 0.1 ~ 1.0 ccm, from the storage container (42) into the raw ingredient solution feeding unit (31) via the compression source (43) and the MFC (41a), and at the same time, the atomizing gas is pumped into the atomizing gas feeding unit (32) at a flow rate of approximately 200 ~ 300 ccm, whereas the shield gas is pumped into the shield gas feeding unit (33) at a flow rate of approximately 200 ~ 300 ccm. The gases within the reaction chamber (61), furthermore, are simultaneously expelled by activating the pressure adjustment device (72). In such a case, the temperature of the shield gas is adjusted in the vicinity of room temperature. The heater (51), furthermore, is adjusted in such a way that the internal temperature of the vaporizer (50) will coincide with the optimal temperature for the ingredient with



the highest vaporization temperature among the aforementioned raw ingredients.

[0031]

As a result, the liquid raw ingredient (34) arrives at the distal end of the raw ingredient solution feeding unit (31) while being stocked within the liquid reservoir (35), and in a case where it becomes subsequently blown out of the nozzle (37), it becomes instantly atomized by the atomizing gas flowing from the atomizing gas feeding unit (32), due to which the misty liquid raw ingredient (34) becomes continuously fed into the vaporizer (50) at a constant flow rate. The misty liquid raw ingredient (34) thus fed into the interior of the vaporizer (50) is then heated and vaporized by the heater (51), as a result of which a raw ingredient gas becomes obtained, and said raw ingredient gas is then fed continuously into the gas diffusion unit (66) via the transportation tube (53). In this case, an adjustment is rendered by using the aforementioned heating mechanism in such a way that the internal temperature of the transportation tube (53) will coincide with the optimal temperature for the ingredient with the highest vaporization temperature among the aforementioned raw ingredients. Moreover, an operation for mixing oxygen with the raw ingredient gas by feeding gaseous oxygen from the oxygen gas feeding source (54) is concomitantly carried out.

[0032]

Next, within the interior of the reaction chamber (61), the raw ingredient gas exported into the gas diffusion unit (66) from

the outlet portion of the transportation tube (53) becomes mobilized, while being concomitantly diffused, toward the reaction & generation chamber (63) side from the gas diffusion unit (66), transmitted through the interior of the reaction & generation chamber (63), and then mobilized along the vicinity of the substrate (65) in such a way that it will become suctioned into the gas exhaustion tube (70). An oxide superconductor thin film can thus be generated by reacting the raw ingredient gas on the upper plane side of the heated substrate (65). After the foregoing film formation operation has been perpetually executed over a certain period, an oxide superconductor (80) which possesses an oxide superconductor thin film of a desired thickness with a stable film quality above the substrate (65) becomes obtained.

[0033]

The aforementioned apparatus for manufacturing an oxide superconductor possesses the liquid raw ingredient feeding device (30) of the aforementioned constitution, and therefore, in a case where the liquid raw ingredient (34) is pumped into the raw ingredient solution feeding unit (31) /6

at a constant flow rate and where the atomizing gas is pumped into the atomizing gas feeding unit (32) at a constant flow rate, the liquid raw ingredient (34) arrives at the distal end of the raw ingredient solution feeding unit (31) while being concomitantly socked within the liquid reservoir (35), whereas in a case where it becomes subsequently blown out of the nozzle (37), it becomes

instantly atomized by the atomizing gas flowing from the atomizing gas feeding unit (32), based on which it becomes possible to feed the misty liquid raw ingredient (34) into the vaporizer (50) continuously at a constant quantitative ratio. In a case where the shield gas is pumped into the shield gas feeding unit (33) at a constant flow rate during the operation for feeding the liquid raw ingredient (34) and atomizing gas into the liquid raw ingredient feeding device (30), furthermore, both the atomizing gas feeding unit (32) and raw ingredient solution feeding unit (31) can be cooled, based on which the liquid raw ingredient (34) flowing within said raw ingredient solution feeding unit (31) can also be cooled, and a premature vaporization of said liquid raw ingredient (34) can thus be prevented. The surroundings of the nozzle (37), furthermore, become shielded by the aforementioned shield gas, based on which the adhesion of the raw ingredient gas to the nozzle (37) and the deposition of the same as the liquid raw ingredient (34) within the vaporizer (50) can be prevented.

[0034]

The apparatus for manufacturing an oxide superconductor equipped with the aforementioned liquid raw ingredient feeding device (30) is thus capable of feeding a constant quantitative ratio of the misty liquid raw ingredient (34) into the vaporizer (50) continuously, and since the raw ingredient gas obtained as a result of the vaporization of said liquid raw ingredient (34) can also be fed continuously into the reaction chamber (61) at a constant quantitative ratio, the fluctuations of the pressure and

temperature of the reaction chamber (61) can be inhibited, and a favorable oxide superconductor thin film with stable film quality and superconductive performances can be formed along the lengthwise direction of the substrate (65).

[0035]

As far as the aforementioned manufacturing apparatus is concerned, furthermore, a misty one is fed into the vaporizer (50) as the liquid raw ingredient (34), and since the vaporizing efficiency can be improved, the rate for feeding the liquid raw ingredient (34) can be elevated, which is advantageous in that the film formation efficiency can be improved.

[0036]

(Application examples)

#### Application Example

An oxide superconductor of the Y-Ba-Cu-O type was prepared according to the following procedures by using the apparatus for manufacturing an oxide superconductor characterized by the constitution shown in Figure 1. One the shape of which is shown in Figures 2 and 3 was employed as the liquid raw ingredient feeding device for the CVD. A solution obtained by solubilizing into diglyme a mixture of  $\text{Y}(\text{thd})_3$ ,  $\text{Ba}(\text{thd})_2$ , and  $\text{Cu}(\text{thd})_2$  characterized by a molar ratio of Y : Ba : Cu = 1.0 : 2.4 : 3.3 was stocked, as a liquid raw ingredient, within the storage container. This liquid raw ingredient was fed, via the

compression source and liquid microscopic MFC, into the liquid raw ingredient feeding unit continuously at a flow rate of 0.2 mL/min. At the same time, Ar was pumped, as an atomizing gas, into the atomizing gas feeding unit at a flow rate of approximately 300 ccm, whereas Ar was pumped, as a shield gas, into the shield gas feeding unit at a flow rate of approximately 300 cc[/min]. It became possible, as a result of the foregoing operation, to feed a constant quantitative ratio of the misty liquid raw ingredient continuously into the vaporizer and also to feed a constant quantitative ratio of the raw ingredient gas obtained as a result of the vaporization of said liquid raw ingredient into the reaction chamber continuously. The respective temperatures of the vaporizer and transportation tube were each designated at 240°C at this stage. It became possible, as a result of the foregoing operation, to feed a constant quantitative ratio of the misty liquid raw ingredient continuously into the vaporizer and also to feed a constant quantitative ratio of the raw ingredient gas obtained as a result of the vaporization of said liquid raw ingredient into the reaction chamber continuously [sic: Duplication].

[0037]

A Y-Ba-Cu-O-type oxide superconductor thin film was formed on a substrate by designating the conditions within the reaction chamber as follows: Substrate transportation rate: 30 cm/h; substrate heating temperature: 760°C; reactor inner pressure: 5 Torr; flow rate of gaseous oxygen from the oxygen gas feeding

source: 50 ~ 100 mL/min. One obtained by forming a YSZ (yttrium-stabilized zirconia) plane-oriented intermediate layer on a Hastello[y] tape based on the ion beam-assisted sputtering method (width: 1 cm x length: ~ 30 cm x thickness: 0.02 cm) was used as said substrate.

[0038]

#### Comparative Example

An oxide superconductor thin film was formed on a substrate by using an apparatus for manufacturing an oxide superconductor equipped with the liquid raw ingredient feeding device of the prior art for the CVD shown in Figure 8 instead of the liquid raw ingredient feeding device for the CVD shown in Figure 2 according to procedures otherwise identical to those of the aforementioned application example.

[0039]

Next, measurement results on the temperature fluctuations at the central portion of the reaction chamber in the aforementioned application example and comparative example are shown in Figure 4. In Figure 4, the solid curve <1> shows the relationship between the time and the temperature of the central portion of the reaction chamber in the application example, whereas the dotted curve <2> shows the relationship between the time and the temperature of the central portion of the reaction chamber in the application [sic: Presumably "comparative"] example. As Figure 4 clearly indicates, the temperature fluctuation of the central

portion of the reaction chamber was  $760\pm 0^{\circ}\text{C}$  in the application example, and thus, absolutely no temperature fluctuation was acknowledged. In contrast, the temperature fluctuation of the central portion of the reaction chamber was  $760\pm 5^{\circ}\text{C}$  in the comparative example, and thus, a temperature fluctuation was acknowledged.

[0040]

In a case where the respective pressure fluctuations within the reaction chamber in said application example and comparative example were investigated, furthermore, the pressure fluctuation was  $5\pm 0$  Torr in the application example, and thus, absolutely no pressure fluctuation was acknowledged, whereas in contrast, the pressure fluctuation was approximately  $5\pm 0.2$  Torr in the comparative example, and thus, a pressure fluctuation was acknowledged.

[0041]

Moreover, measurement results on the thicknesses of Y-Ba-Cu-O-type oxide superconductor thin films formed on the substrate in cases where the rates for feeding the liquid raw ingredient into the liquid raw ingredient feeding device were redesignated within a range of  $0 \sim 1.0$  mL/min. in the aforementioned application example and comparative example are shown in Figure 5. In Figure 5, the solid curve <3> shows the relationship between the liquid raw ingredient feeding rate and the thickness of the Y-Ba-Cu-O-type oxide superconductor thin film in the application example, whereas the dotted curve <4> shows the relationship between the

liquid raw ingredient feeding rate and the thickness of the Y-Ba-Cu-O-type oxide superconductor thin film in the comparative example. As Figure 5 clearly indicates, a linear film thickness gain is acknowledged at a liquid raw ingredient feeding rate of 1.0 mL/min. or below in the application example, and thus, the film formation efficiency can be acknowledged to have become greatly improved. The vaporizing efficiency is improved greatly due presumably to the feeding of a misty liquid raw ingredient into the vaporizer in the application example. In contrast, a film thickness gain failure tendency was acknowledged in the comparative example at a liquid raw ingredient feeding rate of 0.3 mL/min. or higher. The rate for feeding the liquid raw ingredient exceeded the rate for 17

vaporizing the liquid raw ingredient presumably because the liquid droplets of the liquid raw ingredient are subjected to a history of becoming vaporized after they have arrived at the bottom of the vaporizer in the comparative example.

[0042]

Each of the tape-shaped oxide superconductors obtained in the application example and comparative example was coated, over the central portion of said oxide superconductor, with Ag by using a sputtering device, and Ag electrodes were further formed on both edges of the same, whereas upon the completion of the Ag coating operation, a thermal treatment was performed in a pure oxygen atmosphere at 500°C over a 2-hour period, as a result of which a measurement sample was obtained. After each of these samples had



been cooled eventually at 77 K by using liquid nitrogen, the critical current density ( $J_c$ ) along the lengthwise direction of each sample was measured under the pervasion of the external magnetic field 0 T (tesla), and the obtained results are shown in Figure 6. In Figure 6, the solid curve <5> shows the position-specific critical current density of the oxide superconductor obtained in the application example along the lengthwise direction, whereas the dotted curve <6> shows the position-specific critical current density of the oxide superconductor obtained in the comparative example along the lengthwise direction. As Figure 6 clearly indicates, the oxide superconductor obtained in the application example is accompanied by minimal critical current density irregularities along the lengthwise direction, and furthermore, an attribute of  $1.0 \times 10^5$  A/cm<sup>2</sup> (77 K, 0 T) or higher is achieved at every position, and thus, a favorable oxide superconductor thin film with stable superconductive performances can be acknowledged to have been formed along the lengthwise direction of the substrate. In contrast, [the oxide superconductor] obtained in the comparative example was plagued with substantial critical current density irregularities along the lengthwise direction, and the critical current density values were lower than  $1.0 \times 10^5$  A/cm<sup>2</sup> (77 K, 0 T) at certain positions, based on which an oxide superconductor thin film with unstable superconductive performances can be acknowledged to have been formed along the lengthwise direction of the substrate.

[0043]

(Effects of the invention)

As the foregoing explanations have demonstrated, the liquid raw ingredient feeding device for the CVD specified in Claim 1 is constituted to possess a cylindrical and distally tapered raw ingredient solution feeding unit wherein a liquid raw ingredient is scheduled to be fed into the interior thereof and a cylindrical and distally constricted atomizing gas feeding unit which is configured to surround the outer circumference of said feeding unit and which feeds an atomizing gas for atomizing the aforementioned liquid raw ingredient into a gap between itself and the aforementioned raw ingredient solution feeding unit, and therefore, in a case where [said device is] orchestrated on a thin film formation device for forming a film of an oxide material on a substrate based on the CVD method, where a liquid raw ingredient is pumped into a liquid raw ingredient feeding unit at a constant flow rate, and where an atomizing gas is pumped into an atomizing gas feeding unit at a constant flow rate, said liquid raw ingredient continuously arrives at the distal end of the liquid raw ingredient feeding unit, and in a case where the same subsequently becomes blown out of said distal end, it becomes instantly atomized by the atomizing gas flowing from the atomizing gas feeding unit, based on which it becomes possible to feed a constant quantitative ratio of the liquid solution [sic] into the vaporizer continuously.

[0044]

As far as the liquid raw ingredient feeding device for the CVD specified in Claim 2 is concerned, furthermore, a cylindrical shield gas feeding unit is configured to surround the outer circumference of the aforementioned atomizing gas feeding unit, and therefore, in a case where the shield gas is pumped into the shield gas feeding unit at a constant flow rate during the operation for feeding the liquid raw ingredient and atomizing gas into the liquid raw ingredient feeding device, it becomes possible to cool both the atomizing gas feeding unit and liquid raw ingredient feeding unit, based on which the liquid raw ingredient flowing within said liquid raw ingredient feeding unit can also be cooled, and the vaporization of said liquid raw ingredient midway can be prevented. The respective surroundings of the distal end of the liquid raw ingredient feeding unit and the distal end of the atomizing gas feeding unit can, furthermore, be shielded by the aforementioned shield gas, based on which the adhesion of the raw ingredient gas to the aforementioned distal ends and the deposition of the same as a liquid raw ingredient can be prevented.

[0045]

As far as the liquid raw ingredient feeding device for the CVD specified in Claim 3 is concerned, furthermore, a liquid reservoir is additionally configured on the liquid raw ingredient feeding unit, and therefore, even if bubbles, etc. migrate into the liquid raw ingredient, said bubbles, etc. become afloat on the

surface of said liquid raw ingredient being stocked in the liquid reservoir, due to which their arrival at the distal end can be prevented.

[0046]

In a case where the liquid raw ingredient feeding device of the present invention for the CVD is orchestrated on a thin film formation device, therefore, it becomes possible to feed a constant quantitative ratio of a misty liquid raw ingredient into the vaporizer continuously and accordingly to feed a constant quantitative ratio of the raw ingredient gas obtained as a result of the vaporization of said liquid raw ingredient into the reaction chamber continuously as well, due to which the pressure and temperature fluctuations within the reaction chamber can be inhibited, and a favorable oxide thin film with stable performances (e.g., film quality, etc.) can be formed along the lengthwise direction of the substrate. Since the misty liquid raw ingredient is fed into the vaporizer, furthermore, the vaporizing efficiency can be improved, and the rate for feeding the liquid raw ingredient can be elevated, which is advantageous in that the film formation efficiency can be improved.

#### Brief explanation of the figures

Figure 1: A constitutional diagram which shows an example of apparatus for manufacturing an oxide superconductor equipped with the liquid raw ingredient feeding device of the present invention for the CVD.

Figure 2: A diagram which shows a magnified view of the liquid raw ingredient feeding device of the present invention for the CVD shown in Figure 1.

Figure 3: A diagram which shows a cross-sectional view of the A-A line of the liquid raw ingredient feeding device for the CVD shown in Figure 2.

Figure 4: A diagram which shows the relationship between the time and the temperature of the central portion of a reaction chamber.

Figure 5: A diagram which shows the relationship between the rate for feeding the liquid raw ingredient and the thickness of the oxide superconductor thin film.

Figure 6: A diagram which shows the [position-]specific critical current densities of the respective oxide superconductors obtained in the application example and comparative example along the lengthwise direction.

Figure 7: A constitutional diagram which shows an example of apparatus for manufacturing an oxide superconductor equipped with a liquid raw ingredient feeding device of the prior art for the CVD.

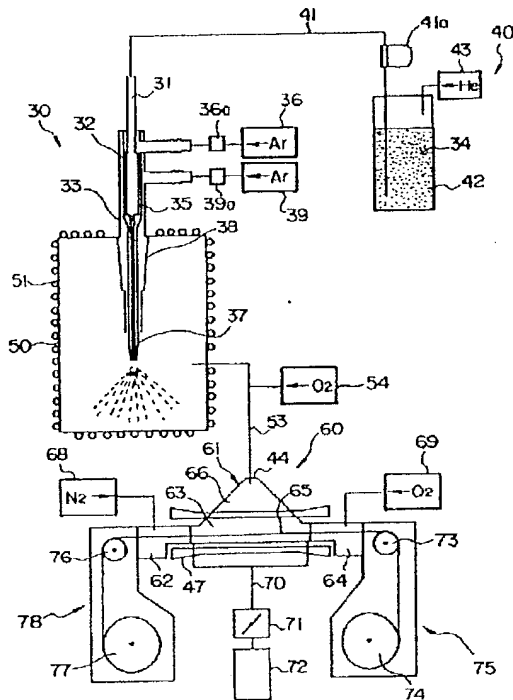
Figure 8: A diagram which shows a magnified view of the liquid raw ingredient feeding device of the prior art for the CVD shown in Figure 7.

Figure 9: A diagram which shows a partial magnified view of the liquid raw ingredient feeding device of the prior art for the CVD shown in Figure 8.

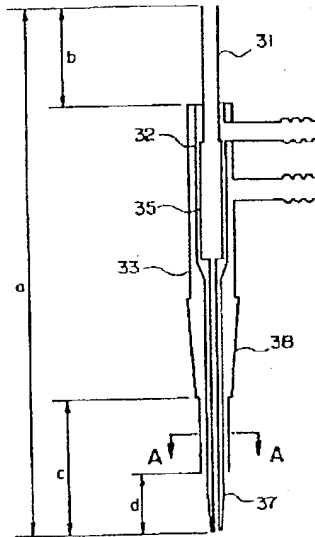
(Explanation of notations)

(30): Liquid raw ingredient feeding device; (31): Raw ingredient solution feeding unit; (32): Atomizing gas feeding unit; (33): Shield gas feeding unit; (34): Liquid raw ingredient; (35): Liquid reservoir.

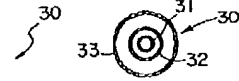
【図1】



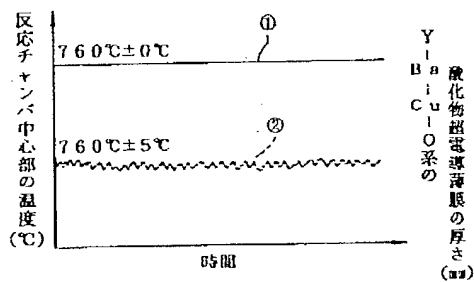
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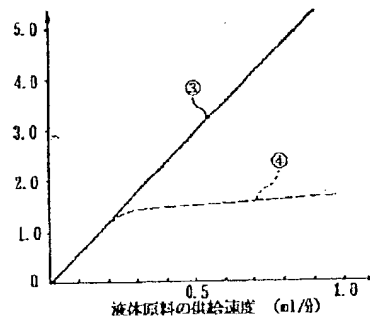
【図3】



【図4】



【図5】



【図9】

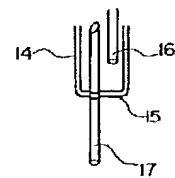


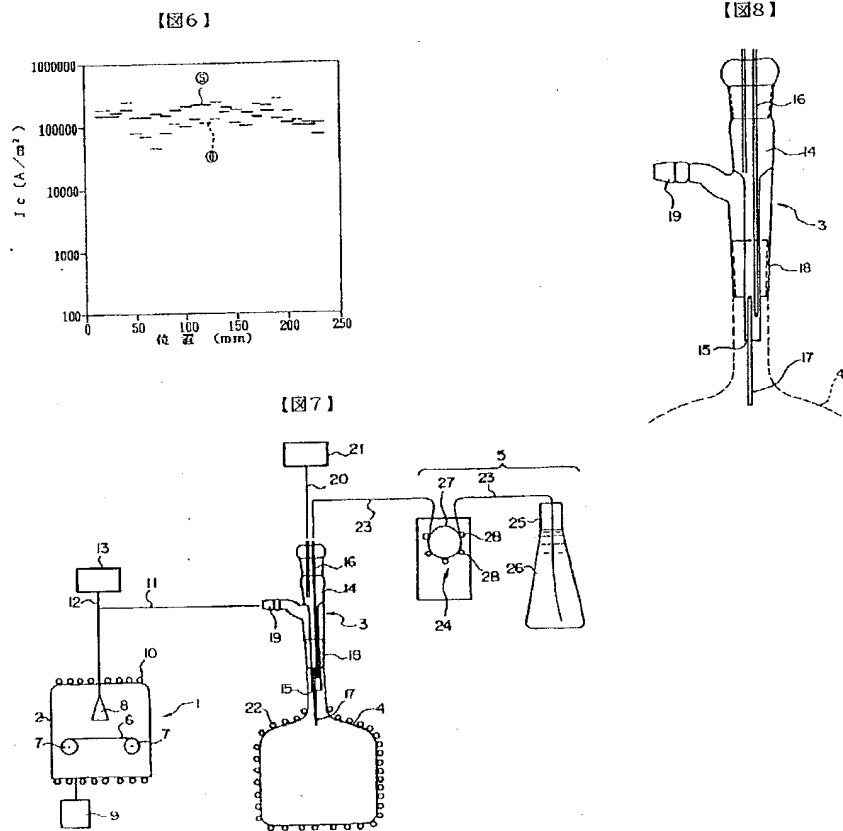
Figure 4

[(1): Temperature of the central portion of reaction chamber (°C);  
(2): Time]

Figure 5

[(1): Thickness of Y-Ba-Cu-O-type oxide superconductor thin film (mm); (2): Liquid raw ingredient feeding rate (mL/min.)]

/9



[(1): Position (mm)]